Investigating the Durability of Electrochemical Sensors for Molten Salts

Investigating the Durability of Electrochemical Sensors for Molten Salts

Hannah J. Levene,[a,b] Ilka Schmueser,[a,b] Ewen O. Blair,[a] Jonathan G. Terry,[a] *Senior Member, IEEE*, Andrew R. Mount,[b] Anthony J. Walton,[a] *Senior Member, IEEE*

[a]Scottish Microelectronics Centre, School of Engineering, [b]School of Chemistry
University of Edinburgh
Edinburgh, UK

***Abstract*—Molten salt is a corrosive, high temperature environment which is extremely challenging for sensing technologies. Microelectrodes are well-positioned as high fidelity electrochemical sensors and previous work has delivered microelectrodes capable of operating in such conditions. However, the lifetime of these sensors requires improvement. This work investigates the origins of device failure.**

Keywords—electrochemical sensor; molten salt; microelectrodes; LiCl-KCl; yield; lifetime; microfabrication

I. INTRODUCTION

The lithium chloride – potassium chloride (LiCl-KCl) eutectic molten salt is a medium of growing importance in several areas of industry, with applications in metal manufacture, renewable energy, and especially nuclear waste reprocessing [1]-[3]. Unfortunately, online analysis of chemical species present in the melt is still challenging; particularly in nuclear reprocessing where monitoring the concentration of uranium (U), plutonium (Pu) and other fission products is invaluable. However, this presents serious engineering challenges, as operating temperatures are typically between 450 and 500°C and the presence of dissolved reactive species result in a highly corrosive environment [4]. Microelectrodes (electrodes with a critical dimension in the tens of micrometres range) are well-documented as effective analytical tools in many areas. They demonstrate enhanced capabilities over macro-scale electrodes such as: a higher signal-to-noise ratio, faster response times, lower susceptibility to convection in the electrolyte, and the ability to reach a steady-state current (enabling the use of simpler, quantitative analytical techniques) [5].

Microfabrication offers many advantages when developing and manufacturing new technologies, including the ability to fabricate many nominally identical devices, control over layout and the capability of systematically altering aspects of the device design. Using such approaches, significant advances have been made in developing microelectrodes for operation in this extreme environment [6]-[8]. These electrodes consist of a metal layer sandwiched between two insulating layers and photolithographically defined windows in the top insulator, which create the contact pad and the microelectrode. Initially, both the yield and lifetime of these microelectrodes was low, with a first time yield of less than 50%. In situ analysis is largely restricted to interpreting the electrochemical signal, as the inherent small size of the sensor and the use of a furnace prevent optical observation. Analysis of samples after removal from the salt is limited due to changes caused by factors such as the electrode cooling to room temperature, salt crystallisation and washing. This makes the identification of failure mechanisms especially challenging.

Previous work utilizing dedicated test structures identified electrical conduction through the underlying silicon dioxide (SiO_2) insulator to the silicon (Si) substrate as the main cause of the low yield and also demonstrated a solution leading to an increase of functioning devices from around 46% to 77% [10, 11]. It needs to be noted that the yield of these electrode designs when used in room temperature aqueous environments is typically 100%, which highlights the challenge of the harsh environment of molten salts.

Despite the resulting improvement in yield, the lifetime of these devices remains not only variable, but limited to the order of hours. If the advantages of microelectrodes are to be realized in an industrial setting, the materials and layout challenges presented by this environment must be addressed. This paper presents the work undertaken to identify the sensor failure mechanisms.

II. DEVICE FABRICATION AND METHODOLOGY

The fabrication procedure for these devices has been detailed in [7] and is only briefly outlined here. A 500 nm thick layer of thermal SiO_2 is grown on a 100 mm Si substrate followed by the deposition of a 100 nm layer of LPCVD silicon nitride (Si_3N_4) forming the underlying insulator. Then either a 50 nm thick layer of platinum (Pt) or 200 nm of tungsten (W) is deposited onto a 20 nm titanium nitride (TiN) adhesion layer. Following patterning of the metal, a second, 500 nm thick, layer of Si_3N_4 is deposited, which is then patterned to provide access to the metal to form the electrode and bond pad. A schematic showing a cross section through the device layers is shown in figure 1.

The authors acknowledge funding from the UK EPSRC through the REFINE consortium (EP/J000779/1) and the PACIFIC project (EP/L018616/1), the EU commission through the FP7 EURATOM ACSEPT (211267) and SACSESS (323282) projects and the SMART Microsystems Programme FS/01/02/10 EPSRC/IeMRC Flagship. H.J.L. acknowledges funding by the EPSRC Centre for Doctoral Training in Integrated Sensing and Measurement.

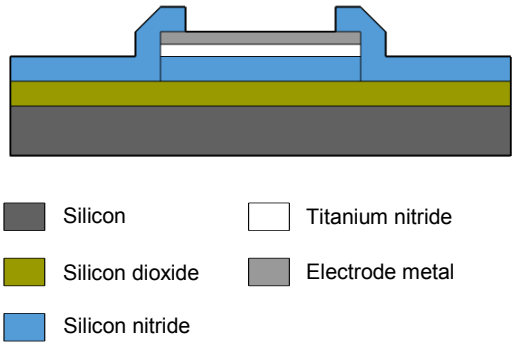

Figure 1. Cross-section of the electrode construction.

Currently, the most important performance factors of the electrodes that need to be determined are their lifetime and yield. For lifetime tests, the device was continuously cycled between electroplating and stripping of silver at 450°C in LiCl-KCl with 5 mM silver chloride (AgCl). One of the most significant characteristics of a microelectrode in electrochemical measurements is that they can reach a scan rate independent steady state current, i_L, for diffusion limited reactions, such as the electroplating of silver. For an inlaid microdisc, this is analytically described by

$$i_L = 4nFDcr \quad (1)$$

where n is the number of electrons in the reaction, F is Faraday's constant, D is the diffusion coefficient, c is the analyte concentration and r is the radius of the electrode [9]. The expression relies on a well-defined electrode geometry, hence any change in the area of exposed metal will result in changes in the current, which is indicative of sensor failure. For the purposes of lifetime determination, only the diffusion-controlled reduction current was analysed, since the oxidation current (solid silver dissolution) is significantly more complicated to model and does not follow equation (1). Typically, a failed device will show non-steady state currents and/or a different order of magnitude current to those analytically predicted.

III. Origins of Failure

Figure 2 shows an initial cyclic voltammetry scan of silver plating and stripping on a 50 µm radius functioning electrode (black) and one where the device is close to failure (red) after nearly 90 minutes of operation. The increase in, and fluctuations on, the signal of the failing electrode suggest changes in the electrode metal as well as dendrite formation when silver electroplating. This change of current prior to failure is shown by both Pt and W electrodes. Imaging of the electrode surface after measurements showed metal removal in the form of small holes and larger missing sections. The failure appears to result from immersion in the melt, occurring irrespective of whether any potential was applied to the device or if it were used for electrochemical sensing. Inspection of the electrode suggests the metal is removed in small sub-micron failure points spread across the entire electrode that appear to merge into larger areas. There are several potential

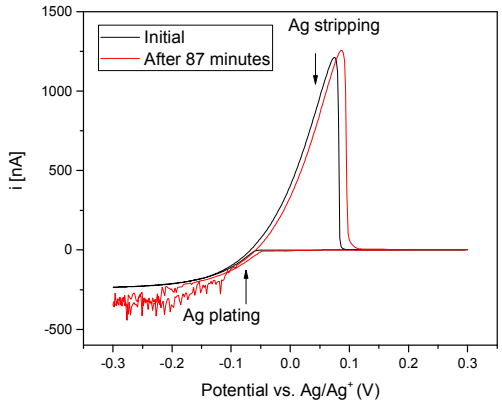

Figure 2. Cyclic voltammetry measurements showing silver electroplating and stripping on a platinum electrode (50 µm radius). Traces show data from the initial scan of a functioning electrode (black) and a scan after 87 minutes when it is about to fail (red).

causes for such metal removal, including chemical dissolution, metal restructuring, pinholes, thermal cracking and attack at grain boundaries. The presence of Ag(I) has been excluded as the cause by testing the devices in melts containing no redox couples. This suggests the plating and stripping process and/or alloying of the electrode with the silver is at least not the main cause of the metal loss, indicating a more fundamental design and/or material problem. Energy-dispersive X-ray spectroscopy on failed samples showed that the surface exposed through the openings in the metal film was the underlying Si_3N_4 insulator, meaning both electrode metal and adhesion layer are removed.

The chemical stability of the W, Pt and TiN were therefore individually tested to determine the cause of the observed metal loss. Considering W and Pt are commonly used as wire and rod electrodes [12,13], it is unlikely that their attack is the source of the metal loss. However, to be certain, their stability was still assessed. This proved challenging since thin films of Pt and W both require adhesion layers, a role currently fulfilled by TiN, and it is difficult to separate the behavior of the adhesion layer from that of the W or Pt. Therefore, bulk corrosion tests were performed by immersing wire samples in 450°C LiCl-KCl and measuring their weight after different durations in the salt. For the W and Pt wire samples, no change in weight was measured over an immersion time of 300 hours. This was also confirmed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) measurements of the salt. The corrosion rate for W and Pt can therefore be assumed to be very small and likely not the limiting factor for device lifetime. However, it should be noted that thin films do not always exhibit bulk properties.

The possibility of thin film TiN corrosion was also investigated using samples of 20 and 200 nm thick sputtered TiN films deposited on 500 nm thick LPCVD Si_3N_4 on a Si substrate. The TiN was patterned as rectangles, Greek cross and split-cross bridge test structures to enable any TiN corrosion to be monitored using resistivity measurements.

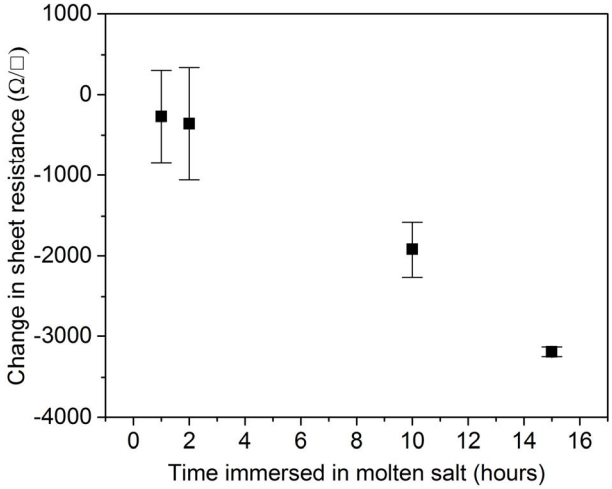

Figure 3. The change of measured sheet resistance (n= 8 individual Greek cross test structures) as a function of time immersed in LiCl-KCl for test structures of 200 nm thick TiN.

The samples were immersed in the LiCl-KCl salt for up to 15 hours. Figure 3 presents the resulting change in sheet resistance *vs.* time as measured using the Greek cross test structures. This actually shows the TiN became more conductive with increasing immersion time, which suggests there is no loss of TiN. Figure 4, which shows an undamaged split Greek cross test structure after removal from the molten salt, backs up this conclusion. If any corrosion had occurred, the sheet resistance would have been expected to increase indicating thinning of the layer. Rather, the resistance has decreased substantially, which suggests that the TiN is not chemically or physically attacked, and the decrease of resistance is likely due to the TiN annealing in the high temperature environment.

To confirm this, samples were annealed at 450°C for 1 hour in an argon atmosphere (following temperature ramp times of 20 minutes (up) and 15 hours (down)), which showed a comparable decrease in sheet resistance to those immersed in the molten salt. These data suggest the mechanism leading to the electrode loss is not predominantly the chemical attack of the electrode metals or adhesion layer.

IV. Conclusions

The origin of failure during operation of microelectrode devices in LiCl-KCl has been established as progressive metal loss for both Pt and W devices with both showing comparable lifetimes. The degree of corrosion of the electrode metal and adhesion layer films in molten salt was tested and corrosion was found to be minimal in each case leading to the rejection of the hypothesis that chemical attack of the metal and/or TiN films triggers device failure and suggests a physical rather than chemical change may be responsible. Further work is required to establish whether the heat treatment during the silicon nitride deposition or molten salt immersion is affecting the corrosion resistance of the conducting layers. Clearly, physical changes are occurring in TiN as is indicated by the decrease in TiN sheet resistance, when exposed to high temperatures.

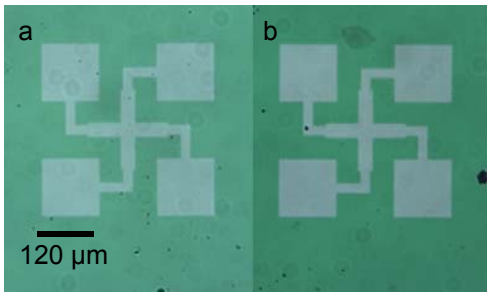

Figure 4. Photograph of 20 nm thick TiN Greek cross test structure (a) before and (b) after 35 hours of immersion in LiCl-KCl at 450°C.

Experimental data presented in the paper are available from http://dx.doi.org/10.7488/ds/2123.

References

[1] Y. Ito and T. Nohira, "Non-conventional electrolytes for electrochemical applications," *Electrochimica Acta*, vol 45, no. 15 – 16, pp. 2611-2622, 2000.

[2] B. Mishra and D. L. Olson, "Molten salt applications in materials processing," *Journal of Physics and Chemistry of Solids*, vol. 66, no. 2-4, pp. 396 – 401, 2005.

[3] D. J. Fray, "Emerging molten salt technologies for metals production," *The Journal of The Minerals, Metals and Mining Society*, vol. 53, no.10, pp. 27-31, 2001.

[4] J. C. Poignet and J. Fouletier, "Physico-Chemical Properties of Molten Salts," *Materials Issues for Generation IV Systems*, pp. 523-536, 2008

[5] J. Heinze, *Angew. Chem., Int. Ed. Engl.*, vol. 32, pp. 1268-1288, 1993.

[6] D. K. Corrigan, E. O. Blair, J. G. Terry, A. J. Walton, and A. R. Mount, 'Enhanced Electroanalysis in Lithium Potassium Eutectic (LKE) Using Microfabricated Square Microelectrodes', *Anal. Chem*, vol. 86, no.22, pp. 11342-11348, 2014

[7] E. O. Blair, D. K. Corrigan, J. G. Terry, A. R. Mount, and A. J. Walton, 'Development and Optimization of Durable Microelectrodes for Quantitative Electroanalysis in Molten Salt', *Journal of Microelectromechanical Systems*, vol. 24, no. 5, pp. 1346 – 1354, 2015.

[8] D. K. Corrigan, J. P. Elliott, E. O. Blair ,S. J. Reeves, I. Schmueser, A. J. Walton, and A. R. Mount, 'Advances in electroanalysis, sensing and monitoring in molten salts', *Faraday Discussions*, vol. 190, pp. 351-366, 2016

[9] Y. Saito, 'A theoretical study on the diffusion current at the stationary electrodes of circular and narrow band types', *Review of Polarography Japan,* vol. 15, pp. 177 – 187, 1968.

[10] E. O. Blair, D. K. Corrigan, H. J. Levene, I. Schmueser, J. G. Terry, S. Smith, A. R. Mount, and A. J. Walton, 'Improving the Yield and Lifetime of Microfabricated Sensors for Harsh Environments', *IEEE Transactions on Semiconductor Manufacturing*, in press.

[11] E. O. Blair, D. K. Corrigan, I. Schmueser, J. G. Terry, S. Smith, A. R. Mount, and A. J. Walton, 'Test structures to support the development and process verification of microelectrodes for high temperature operation in molten salts,' *IEEE International Conference on Microelectronic Test Structures*, pp.158 – 162, 2016.

[12] P. Hébant and G. S. Picard, 'Electrochemical investigations of the liquid lithium/ (LiCl-KCl eutectic melt) interface. Chronopotentiometric and electrochemical impedance spectroscopy measurements.' Electrochemica Acta, vol. 43, pp. 2071-2081, 1998.

[13] B. Prabhakara Reddy, S. Vandarkuzhali, T. Subramanian, P. Venkatesh, 'Electrochemical studies on the redox mechanism of uranium chloride in molten LiCl-KCl eutectic', *Journal of Electroanalytical Chemistry*, pp. 2471-2478, 2004.